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Detection of stress corrosion cracking in u-bend brass specimens by an electro-mechanical method

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DETECTION OF STRESS CORROSION CRACKING IN U-BEND BRASS SPECIMENS BY AN ELECTRO-MECHANICAL METHOD

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A

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ABSTRACT

An apparatus was designed and built which held two u-bend specimens. When the specimens were exposed to a corrodent, losses in strength were detected as a result of stress corrosion cracking. The apparatus was used to study time to failure of cartridge brass u-bend specimens exposed to ammoniacal copper sulfate solutions which varied in pH. A minimum time to failure, 1.06 hours, was detected at pH 7.2. The maximum time to failure, for the range studied, was 28.36 hours at pH 7.7.

No useful data were obtained in the range from pH 6.6-6.8. Thick, black surface coatings were found to be present on the specimens and these were believed to be responsible for the lack of indicated failure.

ACKNOWLEDGEMENTS

The Author would like to express his appreciation to Dr. W. A. Frad for helping to obtain materials and providing advice and assistance with the research. Also, thanks go to Mr. Paul Dowling of Nooter Corporation for supplying the stainless steel necessary in building the apparatus and to Mr. Karl Kaveler of Olin Brass for graciously supplying the brass sheet used in the study.

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I. INTRODUCTION

Detection of stress corrosion cracking in u-bend specimens, not subjected to continuous loading, is in almost all cases accomplished by visual observation. Catastrophic failure is the simplest to detect but it is often desirable to determine cracking without going to this extreme. The ease with which this can be done varies since the crack can range in size from microscopic, just after its initiation, to very large, just short of fracture.

In some cases accurate measurement of time to failure is not important, however, in some tests it is necessary to obtain data which is accurate to the same degree as the other variables considered. This requires that each test be considered as terminated when the cracking has progressed to the same extent. Visually determining whether a crack has progressed to a certain point is largely a matter of interpretation.

To eliminate this problem, as much as possible, it was decided to build an apparatus which would detect the change in strength of a u-bend specimen as a result

of its cracking. When the strength had been reduced to a certain value the apparatus would stop a time recording device and thereby give a representative time to failure measurement.

After having built the apparatus it was used to obtain data from tests in which cartridge brass specimens were totally immersed in ammoniacal copper sulfate solutions with only the pH of the solutions being varied.

II. REVIEW OF THE LITERATURE

A. Apparatus

Various methods of testing materials for susceptibility to stress corrosion while being subjected to tensile forces[1] have been devised. Since the presence of tensile stress is necessary, devices are constructed so as to provide or maintain such a stress in the specimen being tested. The specimen is usually elastically deformed rather than plastically, although the two are often combined. The specimen may be stressed by either of two methods; (1) constant load or (2) constant strain. Constant load testing makes use of weights or springs which place a specimen in tension and maintain the load throughout the test. A specimen tested under constant strain is deformed and merely constrained in that shape while being tested. With regard to both types, Champion said:

> In general, constant load tests are more severe than constant strain tests. When corrosion occurs in the former case, the cross-sectional area of the metal is reduced and the stress per unit area proportionally increased. With constant strain conditions,

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[1] F.A. Champion, Corrosion Testing Procedures (New York: John Wiley & Sons, Inc., 1952) pp. 137-52.

> however, such as a strip bent to a certain form and simply held to that form, corrosion of a general nature would not affect the stress per unit area, although localized corrosion may give a redistribution of stress with considerable reduction of stress in the less corroded parts.[2]

Since there are numerous ways of providing the tensile stress, only a few of the more widely used types will be discussed.

1. Constant load testing

Generally, the methods of testing under constant load have been of the direct loading type, i.e., the specimen is axially loaded in tension by means of weights or springs acting directly in line with the specimen. A typical example of such a mechanism was used by Edmunds, Anderson, and Waring[3] in testing cartridge brass. It consisted of two grips used to hold the ends of the specimen, one attached to a wire running to an upper static support while the other was connected to another wire on which the weights were hung.

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[2]Ibid., p. 138.

[3]Gerald Edmunds, E.A. Anderson, and R.K. Waring, Amer. Soc. Test. Mat.-Amer. Inst. Min. Met. Eng. Symposium on Stress-Corrosion Cracking of Metals (1945) p. 13.

Another type of direct load apparatus was used by Loose and Barbian[4] to test magnesium sheet bars. This unit consisted of a large steel spring which was compressed by tightening a linkage in which the specimen being tested was incorporated. The spring thereby served as the constant load.

Direct tensile loading is obtained when the load is suspended from the end of a lever and the specimen is pulled in tension by the lever at a point near the fulcrum. This method alleviates the necessity for large weights by making use of the mechanical advantage involved. Bulow[5] and Morris[6] utilized this principle in stressing rods made of various copper-base alloys. Morris' apparatus made use of a straight lever with the specimen mounted vertically whereas Bulow's equipment was constructed with an L-shaped lever and the specimen was mounted horizontally. The same principle of

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[4]W.S. Loose and H.A. Barbian, Ibid., p. 276.

[5]C.L. Bulow, Ibid., p. 22.

[6]Alan Morris, "Stress-Corrosion Cracking of Annealed Brasses," Trans. Amer. Inst. Min. Met. Eng., vol. 89 (1930) p. 258.

direct tensile loading was adopted by Hoar and Hines[7] in their study of stress corrosion cracking of 18-8 stainless steel wires.

The primary concern in constructing a piece of apparatus using direct loading or direct tension is to have the force directly in line with the specimen so as not to introduce any bending in it.

The more common constant load devices used for u-bend specimens are based on a simple beam concept. Sager, Brown, and Mears[8] discuss a method commonly termed four point loading where a strip being tested is freely supported at the ends and the load is evenly distributed at two points located symmetrically about the center of the specimen causing it to bow downward.

A large number of the constant load tests mentioned were constructed in such a manner that when catastrophic

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[7]T.P. Hoar and J.G. Hines, Stress Corrosion Cracking and Embrittlement, ed. William D. Robertson (New York: John Wiley & Sons, Inc., 1956) pp. 108-9.

[8]G.F. Sager, R.H. Brown, and R.B. Mears, Amer. Soc. Test. Mat.-Amer. Inst. Min. Met. Eng. Symposium on Stress-Corrosion Cracking of Metals (1945) pp. 256-8.

failure occurred a switch was opened thereby turning off some type of timing device used to record time to failure. This is quite easily accomplished since a weight, a lever, or some type of linkage moves a certain amount upon failure of the specimen and this is sufficient to provide the action for opening a switch.

2. Constant strain testing

As a whole, constant strain devices are simpler both in design and operation. Their sole purpose is to deform a specimen and/or retain it in its deformed state. Unlike constant load testing the apparatus does not provide a continuous force upon the specimen after the initiation of failure. Most of them make use of bending where it is possible such as in the relatively thin materials used for strips. Tests for rods and material with heavier cross sections usually require equipment which can produce pure tensile stress.

A constant strain apparatus for testing rod specimens is discussed by Sager, Brown, and Mears.[9] This particular

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[9]Ibid., p. 262.

unit is made up of four pieces forming a rectangular frame. Nuts threaded onto the ends of the specimen retain the two wedge-shaped end pieces. Because of their shape, the ends are spread apart when the side pieces are forced inward causing the specimen to be placed under tension.

Three point bending was used by Scheil[10] in testing strips cut from stainless steel plate. A small section of rod was located underneath and midway along the length of the specimen. The ends were forced down by means of screws located at each end. A slightly modified test method was achieved by Gohn and Arnold[11] for testing various nonferrous alloys in which they made use of the simple beam principle. The strip was freely supported at each end and then forced downward in the middle by an adjustable screw.

A simple u-bend specimen can be made by applying an axial compressive force on the ends of a strip until it buckles. The force is increased until the desired shape

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[10] M.A. Scheil, Amer. Soc. Test. Mat.-Amer. Inst. Min. Met. Eng. Symposium on Stress-Corrosion Cracking of Metals (1945) p. 396.

[11] G.R. Gohn and S.M. Arnold, Ibid., pp. 160-1.

is attained. Instead of being a simple beam as discussed above the specimen is considered to be a column in which the ends are free, i.e., able to pivot.

Logan and Hessing[12] used an apparatus constructed from a rod which was slightly longer than the undeformed strip and threaded on each end. Two bakelite disks were fitted over the ends of the rod and retained there by nuts. Each end of the specimen was fitted into a slot in the disks. The slot was such that it did not restrict the ends of the specimen from pivoting when bending took place. The nuts were tightened until the desired shape of the specimen had been obtained.

The deformation of the specimen and its retention in that state were both accomplished with Logan and Hessing's apparatus mentioned above. However, in some tests using u-bend specimens the bending action has to be done by hand or by some other means and then placed in the apparatus which merely holds the specimen in that condition. An example of this is a very simple apparatus such as that

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[12]Hugh L. Logan and Harold Hessing, "Stress-Corrosion Tests on High-Strength Aluminum Alloy Sheet," J. Research U.S. Nat. Bur. Stand., vol. 41 (1948) p. 72.

discussed by Dix[13] for testing strips cut from sheet aluminum. The specimen holder consists of a thick sheet of material in which two parallel channels are cut. The distance between the channels can vary depending upon the overall length of the specimens being tested. One end of the specimen is placed in one channel and then bowed sufficiently to allow the other end to be placed in the opposite channel.

In all of the examples of constant strain testing cited so far, no attempt was made to record time to failure by any means other than visual observation. By visually observing the specimens and noting the time elapsed from the start of the test to the time of the first visible sign of failure the person conducting the test could obtain his data.

If catastrophic failure is not desirable, then detecting cracks by visual observation must be relied upon. This type of detection can be hindered by a number of occurrences such as corrosion products on the specimen, the corrosion medium itself if total immersion testing is conducted, and the mere

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[13] E.H. Dix, Jr., "Acceleration of the Rate of Corrosion by High Constant Stresses," Trans. Amer. Inst. Min. Met. Eng., vol. 137 (1940) p. 25.

size of the cracks themselves, to name a few of the more important factors.

Uhlig and Lincoln eliminated the problems noted above by using an apparatus which held a u-bend specimen and by means of a mechanical linkage were able to detect its failure. It is pictured in figure 1. In describing the apparatus, Uhlig said:

> The test apparatus was constructed of . . . stainless steel stock to which was attached a sliding arm of . . . stainless steel strip, both stress relieved. The test specimen was held under stress by a strong compression spring and an adjustable screw located at the top of the holder. Two notched porcelain blocks insulated the specimen itself from the sliding arm. An adjustable screw attached to the sliding arm operated a normal-open microswitch which, in turn, stopped an electric time recorder when the specimen failed.[14]

This piece of test equipment is of the constant strain type even though the specimen would be under a continuous force after initiation of failure. This continuous force would only come into being if the specimen started to weaken from failure and this very action itself would cause termination of the test by opening the microswitch. Subsequent application of force on the specimen would be of no interest.

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[14]H.H. Uhlig and John Lincoln, Jr., "Chemical Factors Affecting Stress Corrosion Cracking of 18-8 Stainless Steels," J. Electrochem. Soc., vol. 105 (1958) p. 326.

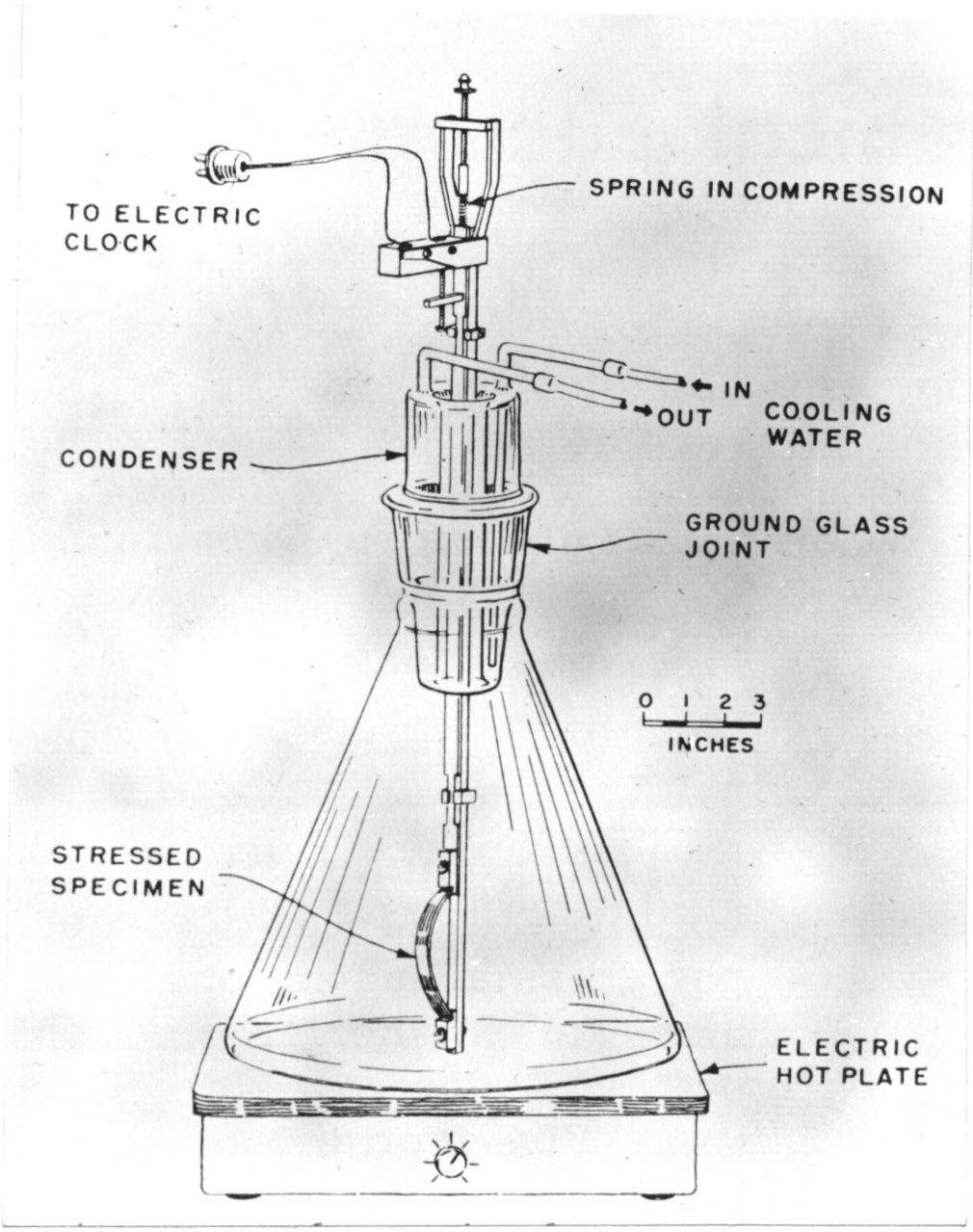

FIGURE 1

UHLIG'S APPARATUS USED TO DETERMINE TIME TO FAILURE OF U-BEND SPECIMENS[15]

[15]Ibid.

B. Corrosion Medium

Copper-base alloys, especially brasses, containing either internal tensile stresses resulting from working or tensile stresses as a result of external forces have two major enemies which produce accelerated cracking, ammonia and mercury. Mercury testing is a quick method to check for stresses but it is not indicative of the conditions to which a material will normally be subjected. Ammonia and its compounds cause cracking in stressed brass. It has been the primary corrodent used in stress corrosion studies since both the vapor and liquid can be used for testing and therefore it more closely approximates service conditions under which the brass will be exposed.

In stress corrosion testing of brass, several variables have been found to be necessary other than ammonia. With respect to some of these variables Morris commented, "It seems that there are four conditions favorable to rapid stress-corrosion cracking: (1) tensile stress, (2) ammonia, (3) oxygen and (4) moisture."[16] Edmunds, Anderson, and

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[16]Morris, op. cit., p. 274

Waring obtained evidence that carbon dioxide was obviously involved when they observed the presence of copper amino carbonate, $Cu(NH_3)_4 \cdot CO_3$, as a corrosion product.[17] This finding then added one more variable to those mentioned by Morris. These variables were not expanded upon until Mattsson[18] found that by changing the pH of an ammoniacal copper sulfate solution he could obtain a varying time to failure of brass specimens. A plot of pH versus time to failure, as it appeared in his work, is shown in figure 2. To this author's knowledge this was the first effort to study stress corrosion of brass at different values of pH, holding other factors constant. Sager, Brown, and Mears, however, had studied essentially the same phenomena in testing magnesium strips exposed to sodium chloride-potassium chromate solutions differing only in pH.[19]

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[17] Edmunds, op. cit., pp. 15-6.

[18] E. Mattsson, "Stress Corrosion in Brass Considered Against the Background of Potential/pH Diagrams," Electrochim. Acta, vol. 3 (1961) pp. 279-91.

[19] Sager, op. cit., p. 269.

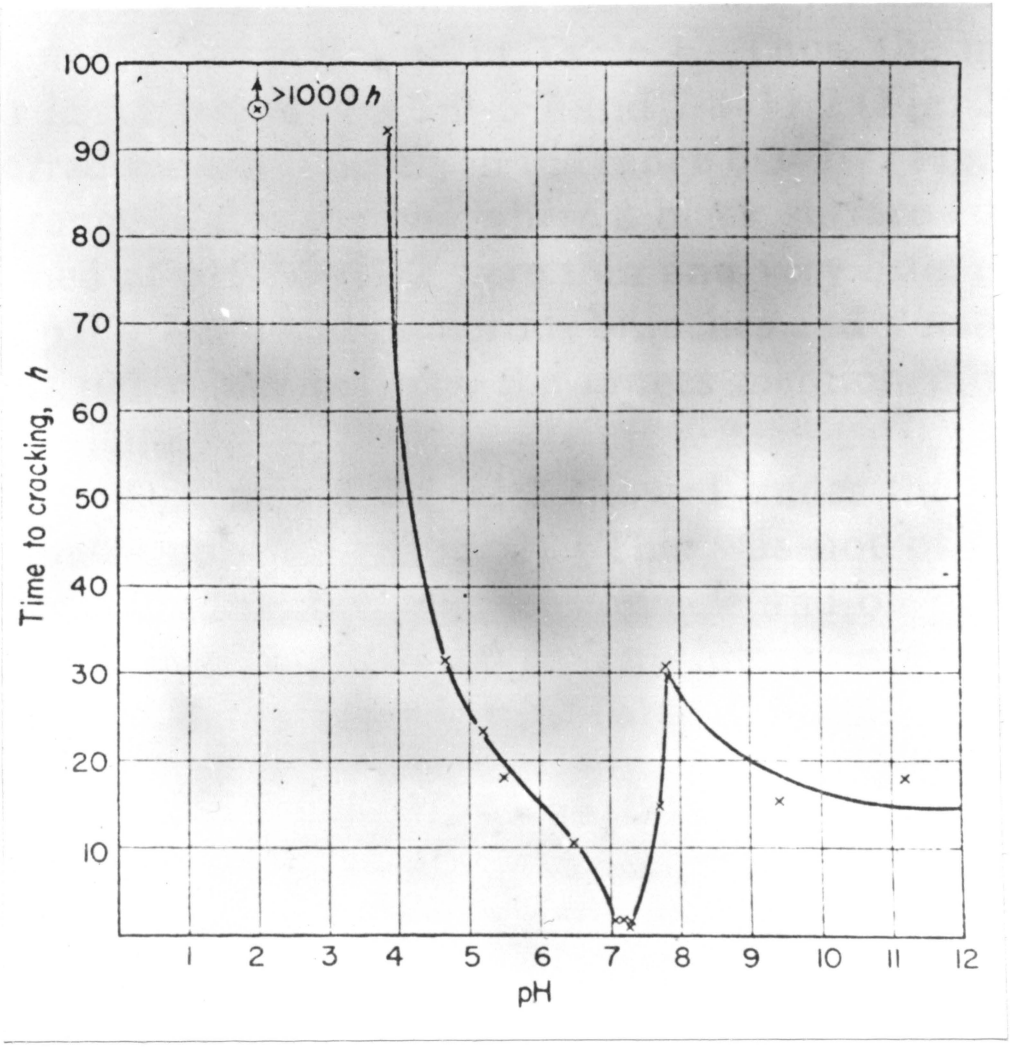

FIGURE 2

TIME TO FAILURE VERSUS pH FOR BRASS U-BEND SPECIMENS AS DETERMINED BY MATTSSON[20] (SOLUTIONS AGED FOR 48 HOURS)

[20]Mattsson, op. cit., p. 284

III. EXPERIMENTAL PROCEDURE

A. Apparatus

The stainless steel apparatus used in the study was built with several goals in mind. One was to try to obtain results which were as exact as possible in terms of time to failure measurements. Another was to test two specimens at the same time so that an average time to failure could be obtained since some of the solutions could age causing a change in both copper content and pH. In order to eliminate the possible sedimentation of precipitate on the tension side of the bend, the specimens were placed with that side down. In constructing the apparatus, material having relatively high strength coupled with excellent corrosion resistance was deemed necessary. Type 316 stainless steel was chosen for these reasons.

Figure 3 shows the stainless steel apparatus with specimens in place. The basic principles of the mechanism were obtained from Uhlig's apparatus (figure 1, page 12), however, the requirements mentioned above demanded a modified system.

The apparatus was constructed so that while holding

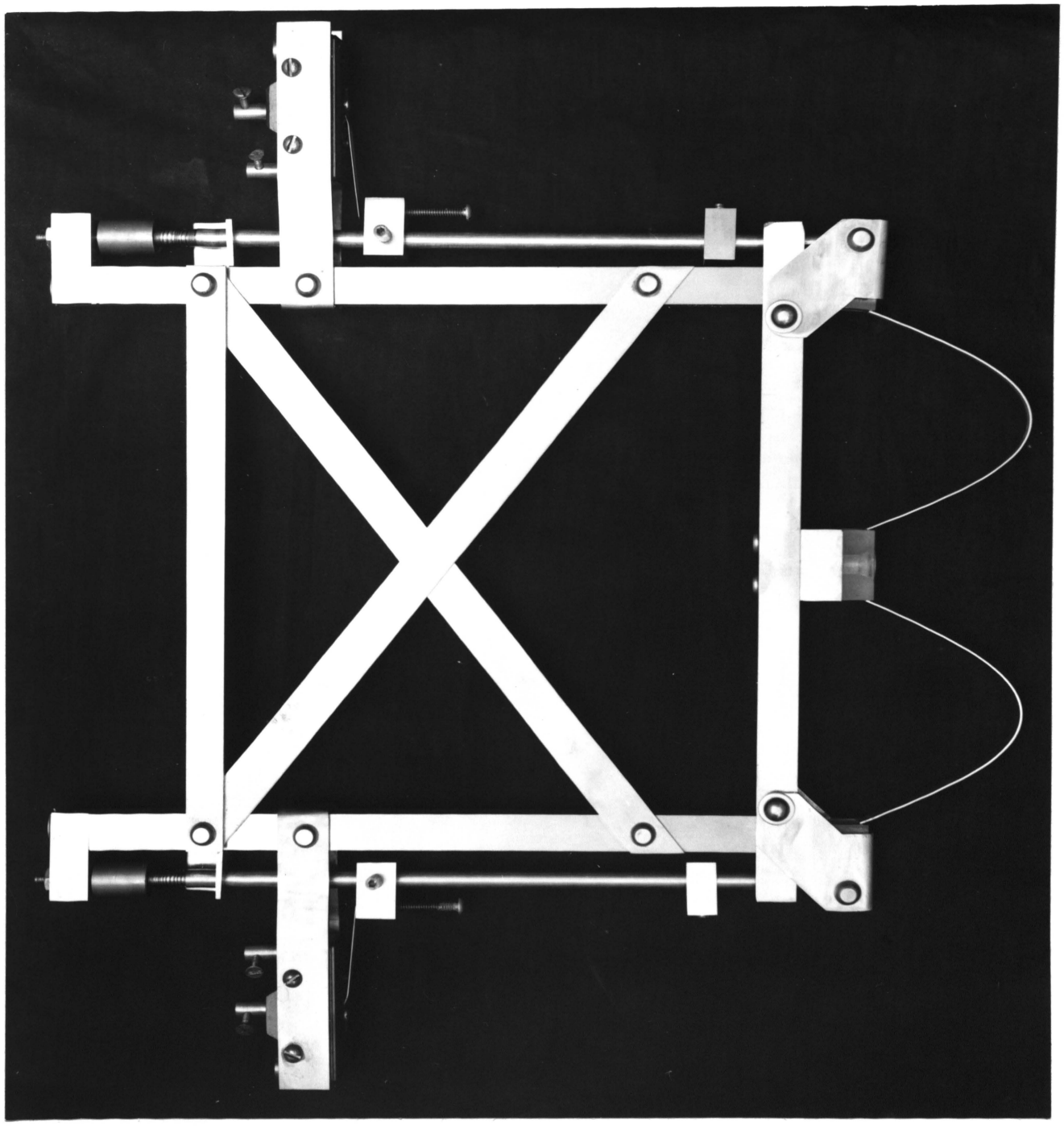

FIGURE 3

STAINLESS STEEL APPARATUS WITH
BRASS SPECIMENS IN PLACE
(REDUCED ONE-HALF)

the specimens and exposing them to the corrosive medium it was able to sense, through its mechanical linkage, a decrease in their strength as a result of cracking. When the loss in strength reached a certain level the apparatus actuated a microswitch which stopped the timers being used to record the amount of time that the specimens had been exposed to the corrodent.

Figure 5 shows a full sectional view of figure 4. The rod, A, pushes on the stainless steel block, B, which is mounted in the pivot housing, C. The pivot housing rotates about rivet, D. The stopblock, E, prevents the rod from traveling beyond a set distance in case the pivot housing swings clear as a result of catastrophic failure on the part of the specimen. The specimen is insulated from the stainless steel by a plastic insert, F. Not shown is a small glass plate which was located on the stainless steel block, B. It served as a hard, smooth surface on which the rod, A, could slide. The glass plate and the tip of the rod were both lubricated to provide smoother operation.

Figure 7 is a partial section of figure 6. The normal-open microswitch is not shown in section but is merely

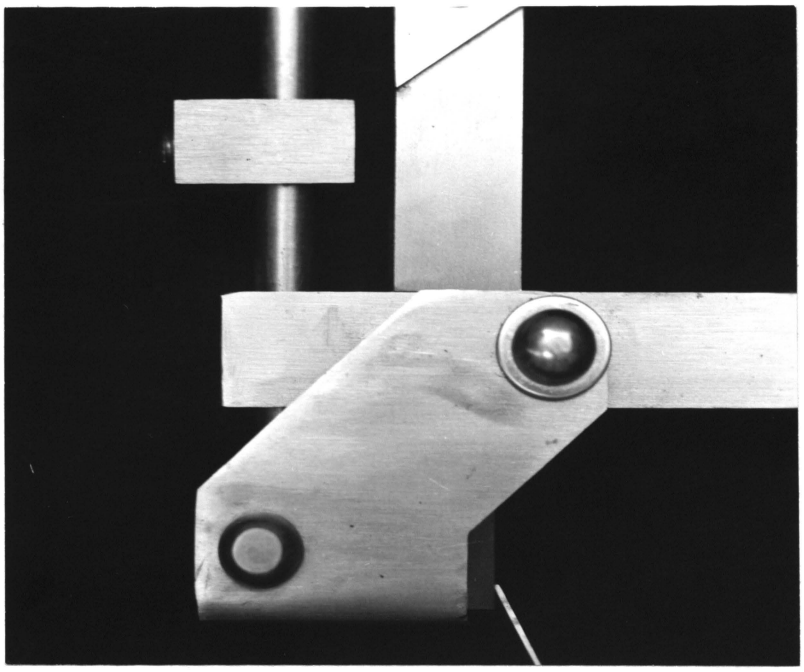

FIGURE 4

CLOSEUP OF PIVOT HOUSING
AND ASSOCIATED LINKAGE
(SAME SCALE AS BELOW)

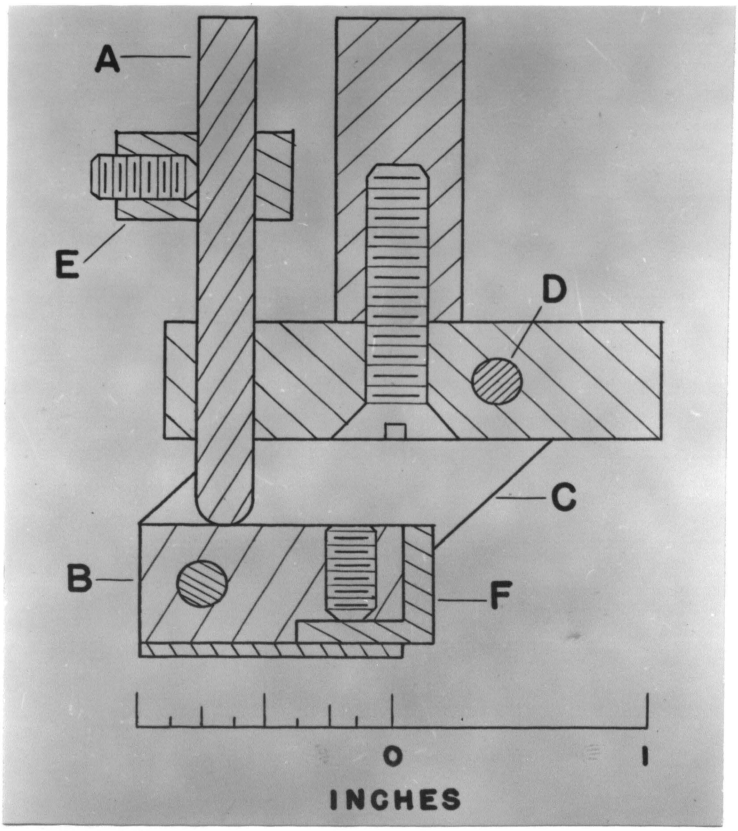

FIGURE 5

SECTIONAL VIEW
OF FIGURE 4

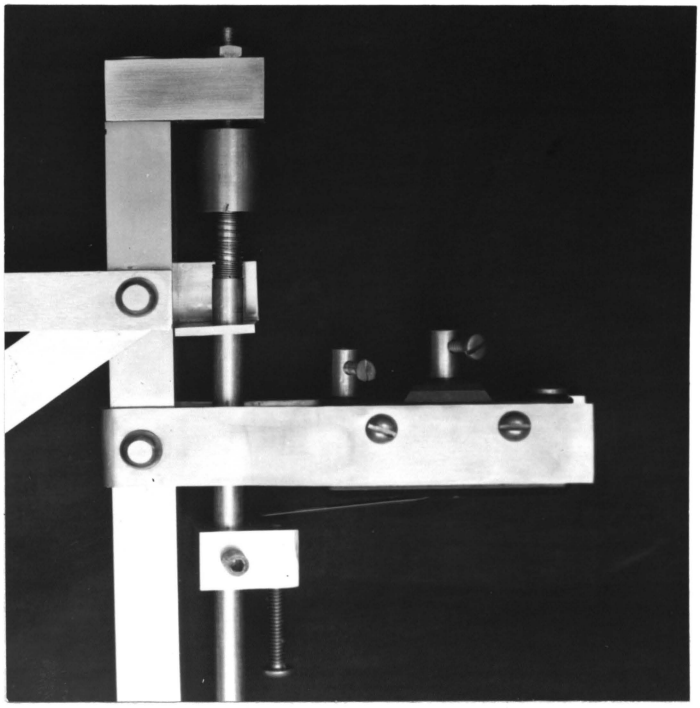

FIGURE 6

CLOSEUP OF LINKAGE ADJUSTMENT SCREW
AND MICROSWITCH ARRANGEMENT
(SAME SCALE AS BELOW)

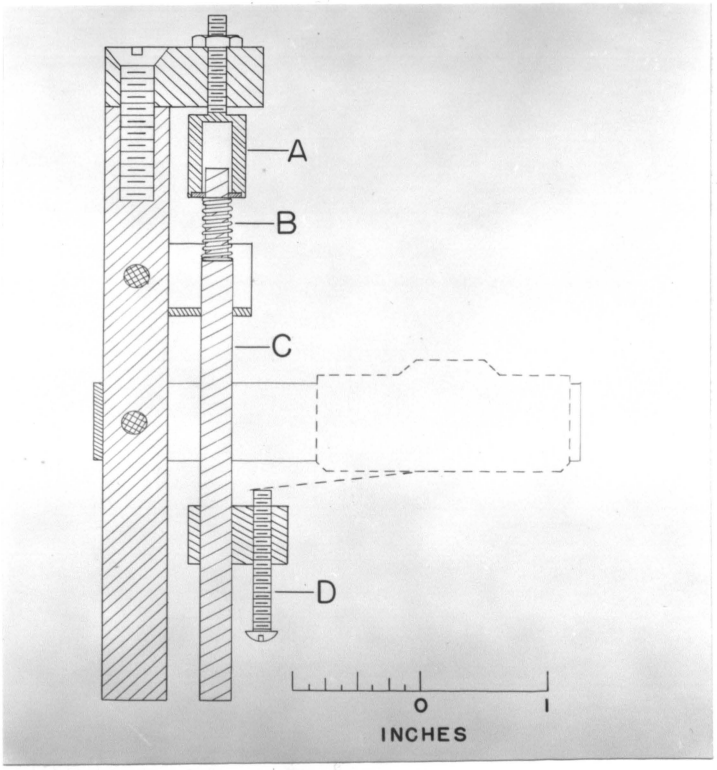

FIGURE 7

SECTIONAL VIEW OF
FIGURE 6

indicated by a dashed outline. Through initial trial runs the setting for the linkage adjustment screw, A, was determined. Having been set it was not changed throughout the entire study. When a specimen was inserted into the apparatus its elastic force was greater than the force offered by the spring, B, and therefore compressed it. When the microswitch adjusting screw, D, was raised to close the microswitch it met a resistance sufficient to move the rod, C, down momentarily. It was further adjusted until the combination of spring force and the force offered by the microswitch was just less than the elastic force of the specimen, which was now flexed to a greater extent thereby resulting in a higher elastic force, whereupon, the mechanism in the microswitch snapped closed.

Incorporated with the apparatus was a piece of plexiglas which acted as a support for the apparatus and also served as a cover for the tank when a run was being conducted, thereby keeping the evaporation losses to a minimum. A layer of modeling clay was placed on the top of the tank to help seal the gap between the plexiglas and the tank. When the apparatus was not in place a piece of plate glass was placed on top of the tank to reduce the evaporation losses.

Figure 8 shows the drying cabinet which was used to maintain a constant temperature condition. The cabinet was constructed with two doors. This allowed the outer door to be opened while the glass inner door remained closed, thus enabling the inside of the cabinet to be observed without disturbing the thermal stability within the cabinet. Figure 9 shows the apparatus in operation as viewed through the glass door. The legs of the cabinet were placed on rubber mats as was the table on which the cabinet was situated in order to reduce the amount of shock which could reach the cabinet from external sources. Also the tank was placed on a foam rubber mat to reduce shock.

The panel on top of the cabinet consisted of dual controls and timers, one for each bank. The switches on the panel together with the microswitches which were mounted on the apparatus controlled the timers used to record the elapsed time from the moment the specimens were first exposed to the corrosive medium until failure of the specimens took place. The control panel and a schematic drawing are shown in figures 10 and 11, respectively. Each bank consisted of a power lead which ran to a microswitch and then to a main power switch. From there it went to a selector switch from

FIGURE 8

CONSTANT TEMPERATURE CABINET WITH
ASSOCIATED CONTROL PANEL

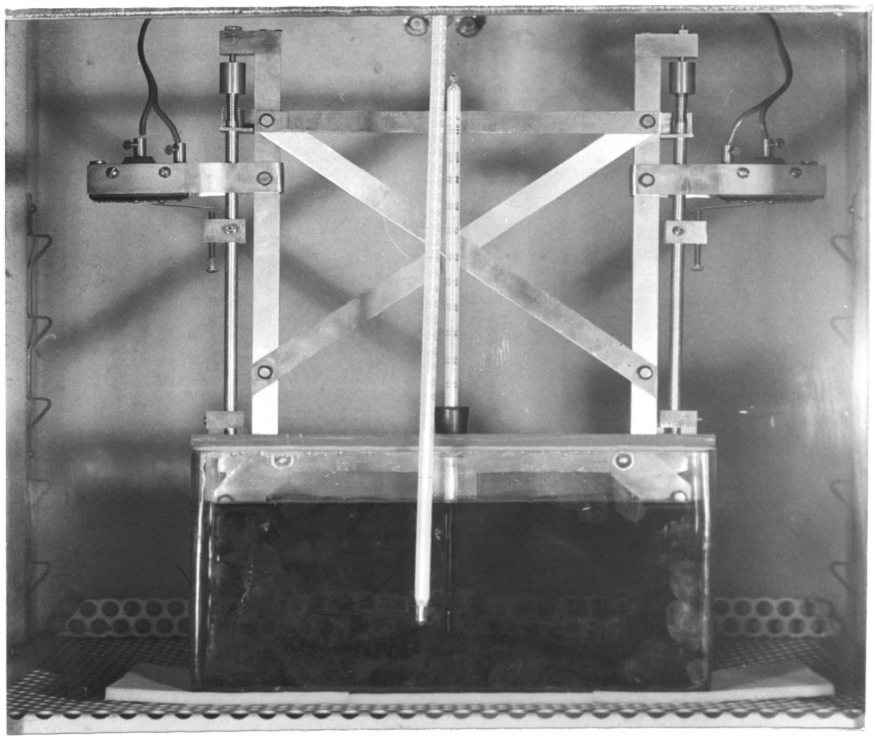

FIGURE 9

APPARATUS OPERATING INSIDE CABINET
AS SEEN THROUGH GLASS DOOR

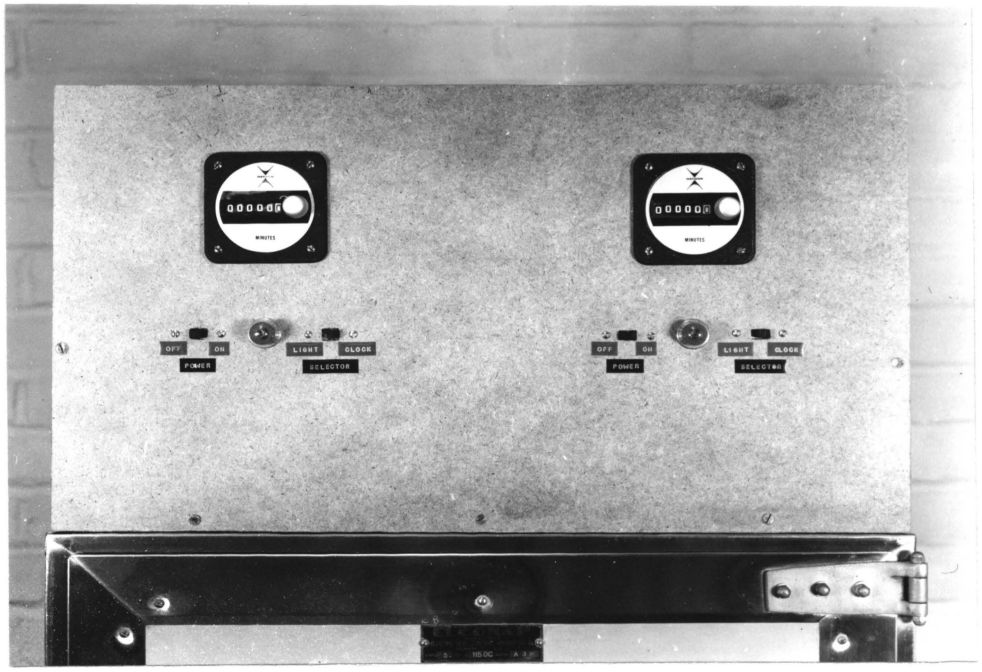

FIGURE 10

CLOSEUP OF CONTROL PANEL SHOWING SWITCHES AND ELAPSED TIME INDICATORS

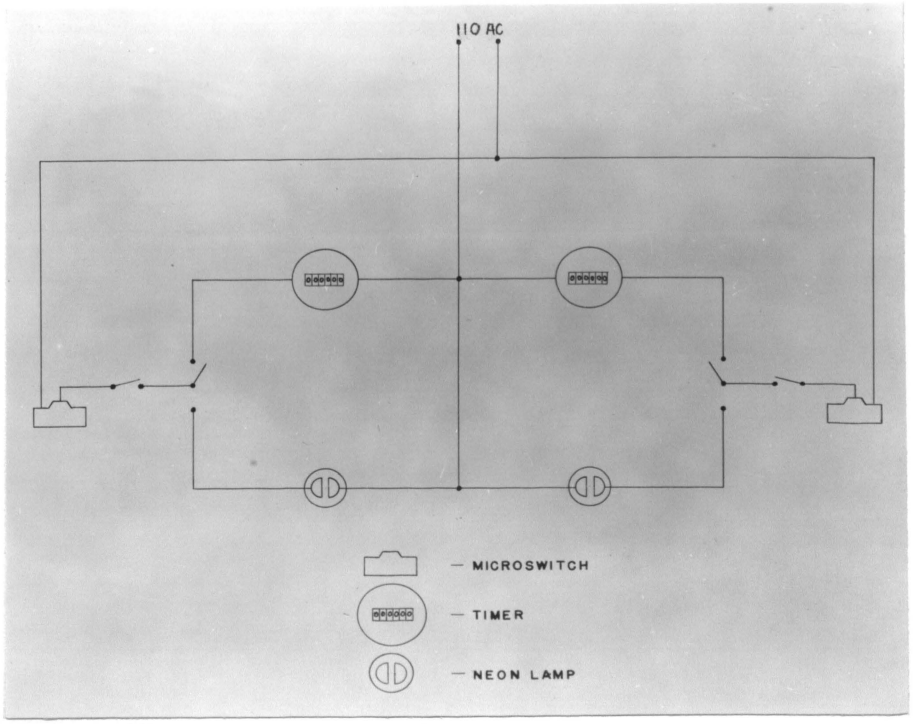

FIGURE 11

SCHEMATIC DRAWING OF ELECTRICAL CIRCUITS IN CONTROL PANEL

which the current was directed to the timer or to a neon lamp. The neon lamp was utilized as a check on the status of the microswitch. Prior to starting each run the selector switch was placed in the "light" position which gave an indication of whether the microswitch was open or closed without disturbing the timer.

Two thermometers were utilized in maintaining the proper temperature conditions. One thermometer was placed through a hole in the plexiglas cover incorporated with the apparatus in order to measure the temperature of the solution while the tests were being conducted. The other thermometer was suspended from the top of the cabinet with its bulb in the general vicinity of the glass tank. The air temperature was held at approximately 36.5°C which in turn kept the solution's temperature at 35±1°C.

B. As-received Stock

The material studied was cartridge brass sheet which had received a half-hard rolled temper. The final rolled thickness was 0.025 inch.

The chemical composition of the brass sheet as analyzed by the supplier was as follows:

Cu - 69.4 %

Pb - 0.02

Fe - $\leq$0.05

Sn - $\leq$0.05

P - nil

Mn - nil

Ni - $\leq$0.04

Ag - $\leq$0.02

Zn - balance

The sheet had a hardness of 15-T 85.7 and had an average grain size of 0.035 millimeters when estimated in accordance with the ASTM standards using the Heyn intercept method.[21]

A three dimensional layout composed of representative photomicrographs of the rolling plane, longitudinal, and transverse sections is shown in figure 12.

C. Preparation of Specimens

The specimens were sheared with the longitudinal axis

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[21]"Estimating the Average Grain Size of Metals." ASTM designation: E112-63, 1964 Book of ASTM Standards, American Society for Testing and Materials, Part 31, 1964, p. 234.

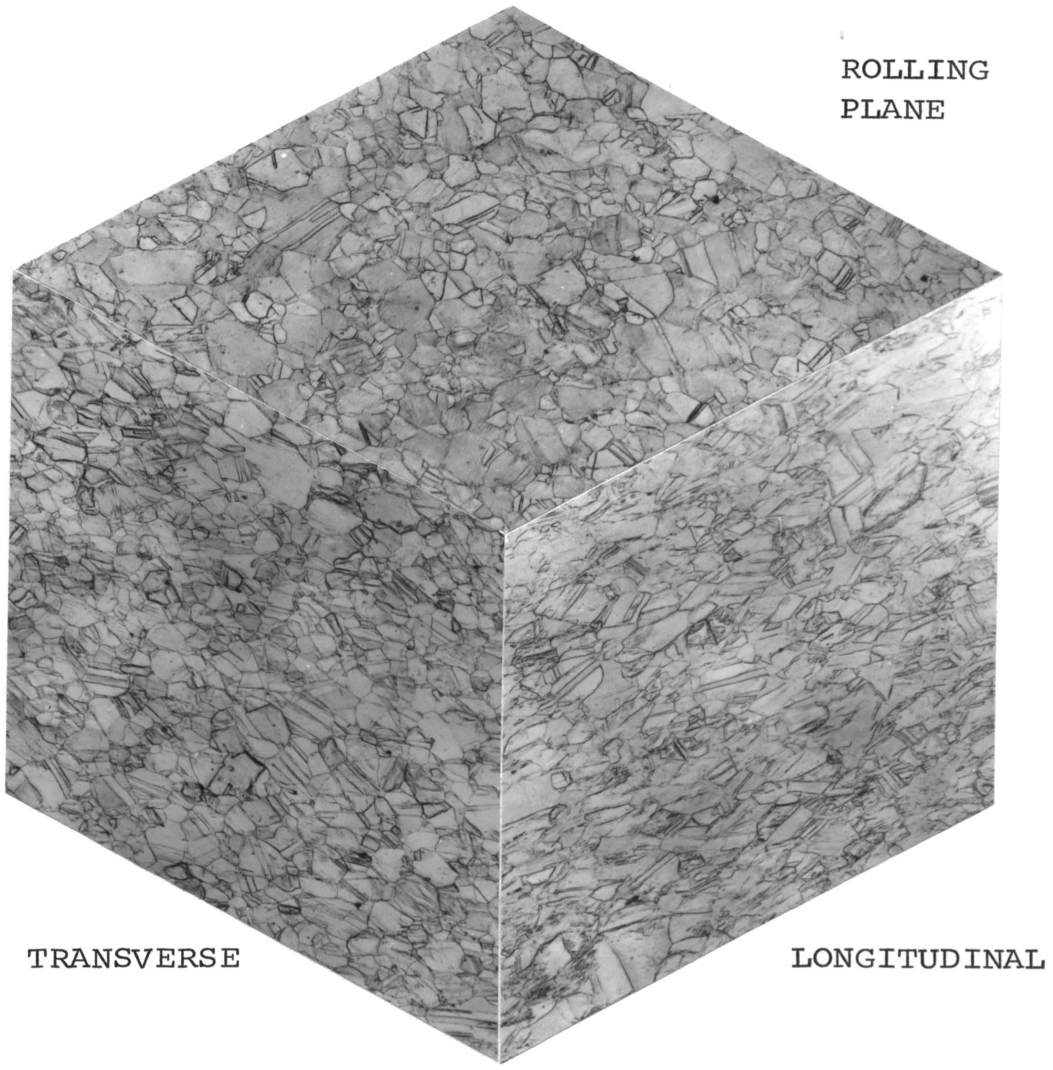

FIGURE 12

THREE DIMENSIONAL LAYOUT OF
AS-RECEIVED MATERIAL
(150X, $FeCl_3$ ETCH)

parallel to the direction of rolling and then dressed on 400 and 600 grinding paper, respectively, until the width was 0.250±0.001 inch. The final dimensions obtained were 5.0 x 0.250 x 0.025 inches. They ranged in weight from 4.20 to 4.40 grams.

The handling of the brass sheet and the subsequent handling of the sheared strips resulted in fingerprints and stains which were quite tenacious. Rinsing with various organic solvents failed to remove them. Pickling with dilute acids resulted in a differential attack with the unstained portion being attacked to the greatest extent. It was decided to use a polish to remove the stains and provide a continuous surface unobstructed by any formation which would not allow wetting by the corrosion medium. The polish used was Brasso, a commercial product used for cleaning and polishing brass. A piece of cotton wetted with the polish was used to remove the fingerprints and stains. The polish was allowed to dry and then the strips were polished with tissue paper to remove the residue. In order to remove any soluble film resulting from the polishing, the strips were placed in a bottle containing trichloroethylene and allowed to soak until an unbroken

film of the solvent adhered to them. The strips were then placed in a desiccator and stored until just prior to testing when they were removed and bent.

The next step in the preparation of the specimens consisted of placing the strips in a vise and closing the jaws to a gap of two inches. Figures 13-16 show a strip being bent in steps in order to give an indication of the amount of elastic stress present in the flexed strip as compared to its final shape when released. Figure 17 compares the unbent strip with the bent specimen and shows that the final span across the ends of the bent specimen is approximately 3 7/8 inches. Reproducibility was found to be very good since specimens could be laid edge to edge with the geometry of the bend corresponding over the entire length.

D. Preparation of Solutions

The corrosion medium was composed of $CuSO_4 \cdot 5H_2O$, $(NH_4)_2SO_4$, and NH_4OH. Each solution contained the same amount of copper sulfate, which corresponded to 0.05 gram atom of copper per liter. The ammonium sulfate and the ammonium hydroxide were added in different amounts in order

FIGURE 13

SPECIMEN POSITIONED IN VISE
PRIOR TO BENDING

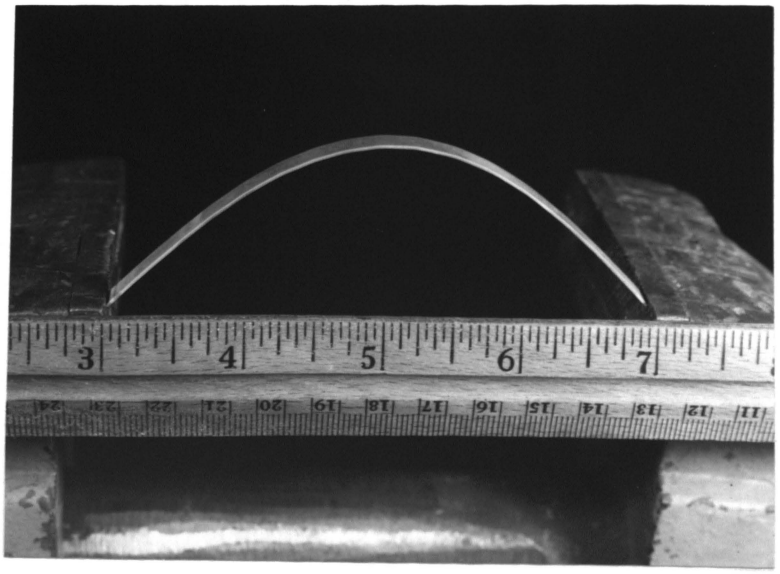

FIGURE 14

SPECIMEN COMPRESSED
TO FOUR INCH SPAN

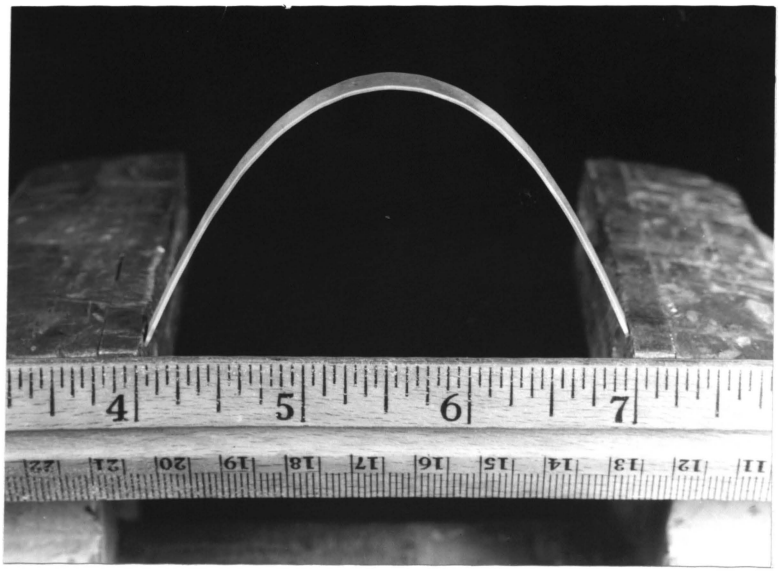

FIGURE 15

SPECIMEN COMPRESSED
TO THREE INCH SPAN

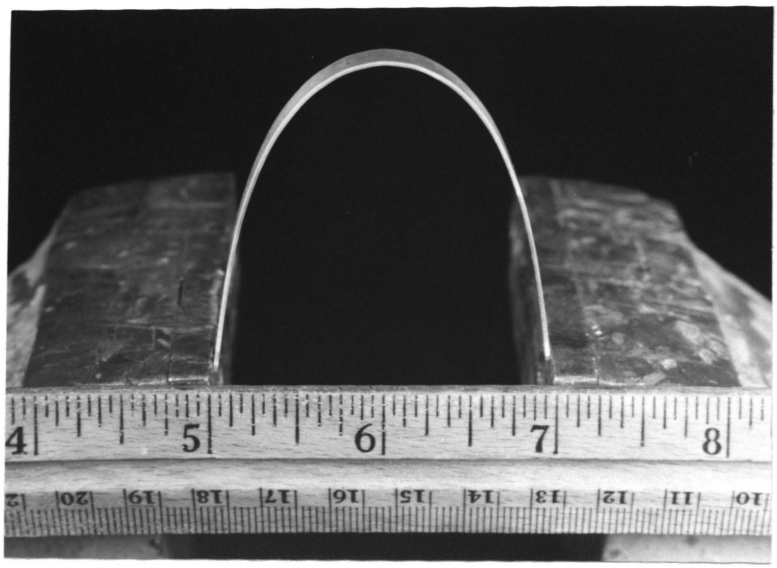

FIGURE 16

SPECIMEN COMPRESSED
TO TWO INCH SPAN

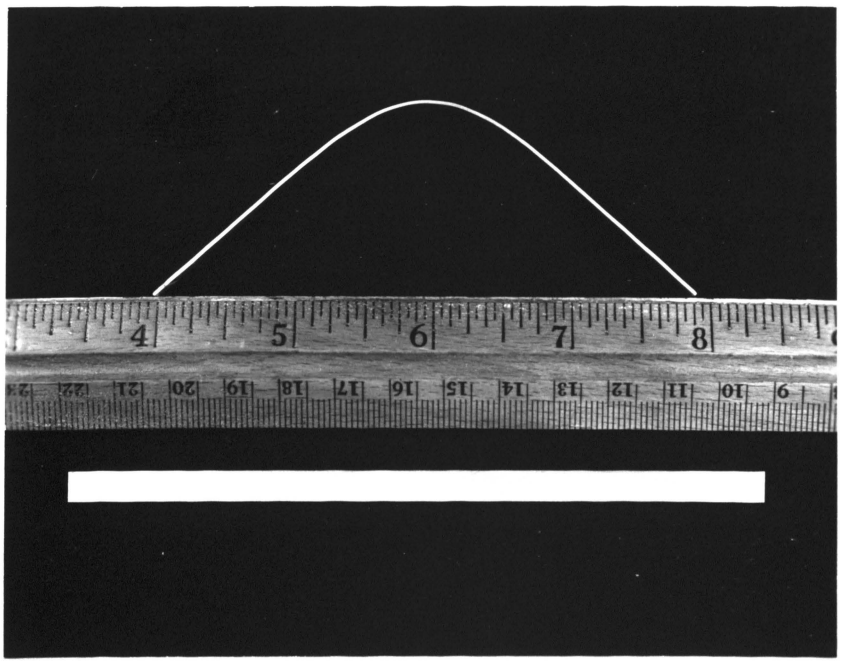

FIGURE 17

COMPARISON BETWEEN UNBENT STRIP
AND FINISHED SPECIMEN

to vary the pH but the total ammonia content always corresponded to one gram mole of ammonia per liter. The volume of the solution was 3.2 liters. Distilled water and reagent grade chemicals were used in preparing all solutions. The distilled water was prepared in a glass distilling apparatus.

The ammonia content in the ammonium hydroxide was determined by means of specific gravity measurements using a hydrometer graduated in divisions of 0.001 unit. The specific gravity of the ammonium hydroxide used in the preparation of the solutions was 0.9500. A hydrometer cylinder was partially filled with a stock ammonium hydroxide solution and then concentrated ammonium hydroxide was added until a specific gravity of 0.9500 was attained.

Prior to mixing each solution a volume of distilled water in excess of that necessary was tested for pH. The distilled water generally had a pH between five and six. In order to have a common starting point the water was brought to pH 5.0 by adding sulfuric acid. Usually no more than two or three drops of dilute sulfuric acid were necessary to obtain pH 5.0. By this means the reproducibility of the solutions was assured as was the correlation between solutions.

The copper sulfate was weighed with an analytical balance and the ammonium sulfate was weighed with a triple beam balance. The copper sulfate and the ammonium sulfate were then mixed individually in one liter volumetric flasks and then heated to 35°C before they were poured into the tank. The ammonium hydroxide was then prepared and added with sufficient water to complete the 3.2 liter volume. A cover was placed on the tank to reduce evaporation.

One hour after preparation of the solution a twenty-five millimeter aliquot was obtained and a pH measurement was made. The one hour delay allowed any precipitate which might form upon mixing to settle and not be present in the aliquot or affect the pH. The first test of specimens was conducted twenty-four hours after preparation of the solution.

For a detailed explanation of the calculations which were necessary in preparing the solutions, the reader is directed to the appendix at the end of this thesis.

E. Procedure for Testing

After being bent the specimens were weighed on an analytical balance to within one-tenth of a milligram, using calibrated weights, and then placed in the stainless steel apparatus.

Before the run was started a twenty-five milliliter aliquot was extracted from the tank making sure that the pipette tip was in the region where the specimens would be located. This was to insure that no precipitate except that present in suspension at the time the aliquot was obtained would be secured in the sample.

After extracting the aliquot a pH determination was made of the whole volume remaining in the tank. The solution was stirred with the electrode but in such a manner as to minimize the possibility of disturbing any precipitate present.

Because the specimens had to be immersed before the connections to the microswitches could be made it was found necessary to record four minutes on the timers prior to testing. When the specimens were ready to be immersed a stop watch was started and allowed to run for five minutes. At the end of the first minute the apparatus was set in place, the electrical connections made, and the microswitches closed by means of adjusting screws. When the stop watch reached five minutes the timers were started and allowed to run until failure occurred and the microswitches opened.

After failure had occurred the power switches were turned off and the leads to the microswitches disconnected. The apparatus was then withdrawn and the specimens were removed and washed with a stream of distilled water. As much of the residue, precipitate and other loose material was removed by the stream as possible. All tenacious coatings were left intact. The strips were than rinsed with methanol, dried with warm air and placed in a desiccator. The specimens were weighed and the weight losses recorded. The left bank specimen was left intact, labeled with a sticker bearing the run number and stored in a desiccator so that it could be referred to if necessary for further information at a later time. The right bank specimen was cut into three sections with the major portion of the bend being mounted and metallographically prepared. The remaining pieces were placed in a vial labeled with the run number and placed in a desiccator for possible future observations and/or tests.

F. Copper Titration

The determination of copper by titration made use of the iodine-thiosulfate reaction. Prior to testing the specimens a twenty-five milliliter aliquot was taken from the tank and placed in a 250 milliliter Erlenmeyer flask.

Two or three milliliters of glacial acetic acid were added to preclude the possibility of a precipitate forming on the sides and bottom of the flask. The titration was usually conducted only after three or four samples had been collected over a period of several days.

The normality of the thiosulfate was found to be 0.1322 meq/ml when titrated against three samples of potassium iodate. The thiosulfate was also standardized against copper metal and found to have the same normality.

G. pH Measurements

The pH measurements were made with a Beckman pocket pH meter. The combination electrode was considered to be an advantage over a dual electrode arrangement because it could be used to stir the solution while making the measurement since stirring is necessary with a weakly buffered solution. Standardization was made with a standard buffer solution having a value of pH 7.00. Temperature correction factors[22] were not necessary because they were too small to affect the readings since the accuracy to which the meter

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[22] Beckman Pocket pH Meter Instruction Booklet. Bulletin 534-A, pp. 18-9.

could be read was 0.1 pH unit.

H. Metallography

The specimens were mounted using either thermosetting or thermoplastic material. The thermoplastic mount(Lucite) was found to be the best because it virtually eliminated capillary attraction which occurred between the specimen and the mount causing the edges of the specimen to become stained by the trapped etching reagent. After mounting, the specimens were prepared on 4/0 dry metallographic grinding paper and then polished by swabbing with a piece of cotton wetted with an alcohol-based ferric chloride solution. The swabbing action was done with firm pressure.

Two etchants, each accenting different features, were used. The as-received material was etched with the aqueous ferric chloride etchant because it produced a good contrast between the grain boundaries and the grains. This facilitated the grain size determination. The test specimens were etched with an ammonium hydroxide-hydrogen peroxide etchant since it gave contrast between individual grains rather than emphasizing the grain boundaries thereby allowing the cracks to be seen more easily. Table II in the appendix lists the

polishing and etching reagents mentioned in this section.

All of the photomicrography was done on a Bausch and Lomb research metallograph using sheet film.

IV. RESULTS AND DISCUSSION

A. Time to Failure

It was originally proposed that runs would be conducted from pH 6.5 through 7.5, in increments of one-tenth pH unit, with the primary aim being to investigate the region where Mattsson had reported finding a minimum time to failure. Figure 2 on page 15 is a plot of Mattsson's data showing a minimum occurring in a range from 7.0 to 7.3.

Table I gives the sequence used in covering the range under consideration. Runs 1-8, 11, 13, 14, 16, and 17 yielded time to failure results. Figure 18 shows a plot of time to failure versus pH. The minimum time to failure, 1.06 hours, occurred at pH 7.2. Time to failure values increased sharply at pH 7.5 and resulted in a maximum, for the range studied, of 28.36 hours at pH 7.7. Values were obtained for all of the increments from pH 6.9-7.7. However, the runs that were carried out on the acid side gave no results except for some of the pH 6.9 runs. Because of the difficulties encountered in this range the characteristics of the solutions will be discussed in order to provide an explanation for this observed behavior.

TABLE I

EXPERIMENTAL DATA

Run No.	pH 1 hr	pH 24 hr	copper in solution (percent) 1 hr	copper in solution (percent) 24 hr	average time to failure (hours)	average weight loss (mg)	average weight loss rate (mg/hr)
1	6.9	7.1	87.10	71.69	1.42	19.4	13.9
2	7.0	7.0	98.74	97.16	1.12	9.6	8.5
3	7.1	7.1	100.00	98.74	1.18	10.9	9.2
4	7.3	7.3	100.00	100.00	1.43	25.9	18.1
5	7.7	7.7	100.00	100.00	28.36	912.4	32.1
6	7.4	7.4	100.00	100.00	2.53	50.1	19.7
7	7.5	7.5	100.00	100.00	7.64	274.2	31.6
8	7.6	7.6	100.00	100.00	19.21	650.1	33.8
9	6.5	6.7	51.57	27.04	DNF52*	88.8	1.7
10	6.7	6.9	42.13	32.70	DNF48	122.1	2.5
11	6.7	7.0	49.68	29.55	1.60	6.1	3.8
12	6.5	6.6	38.05	20.44	DNF48	66.4	1.3
13	6.7	6.9	42.13	30.50	1.71**	71.7	3.0
14	6.8	7.0	71.38	43.71	1.50	9.6	6.4
15	6.6	6.8	55.97	32.70	DNF48	114.3	2.4
16	7.2	7.2	100.00	99.37	1.06	12.5	11.7
17	6.7	6.9	44.96	34.90	1.67	8.0	4.7
18	6.5	6.7	54.40	27.40	DNF48	90.6	1.9
19	6.6	6.8	50.62	32.07	DNF48	144.7	3.0

* Did not fail within 52 hours

** One specimen failed at time shown while the other specimen did not evidence failure after 48 hours

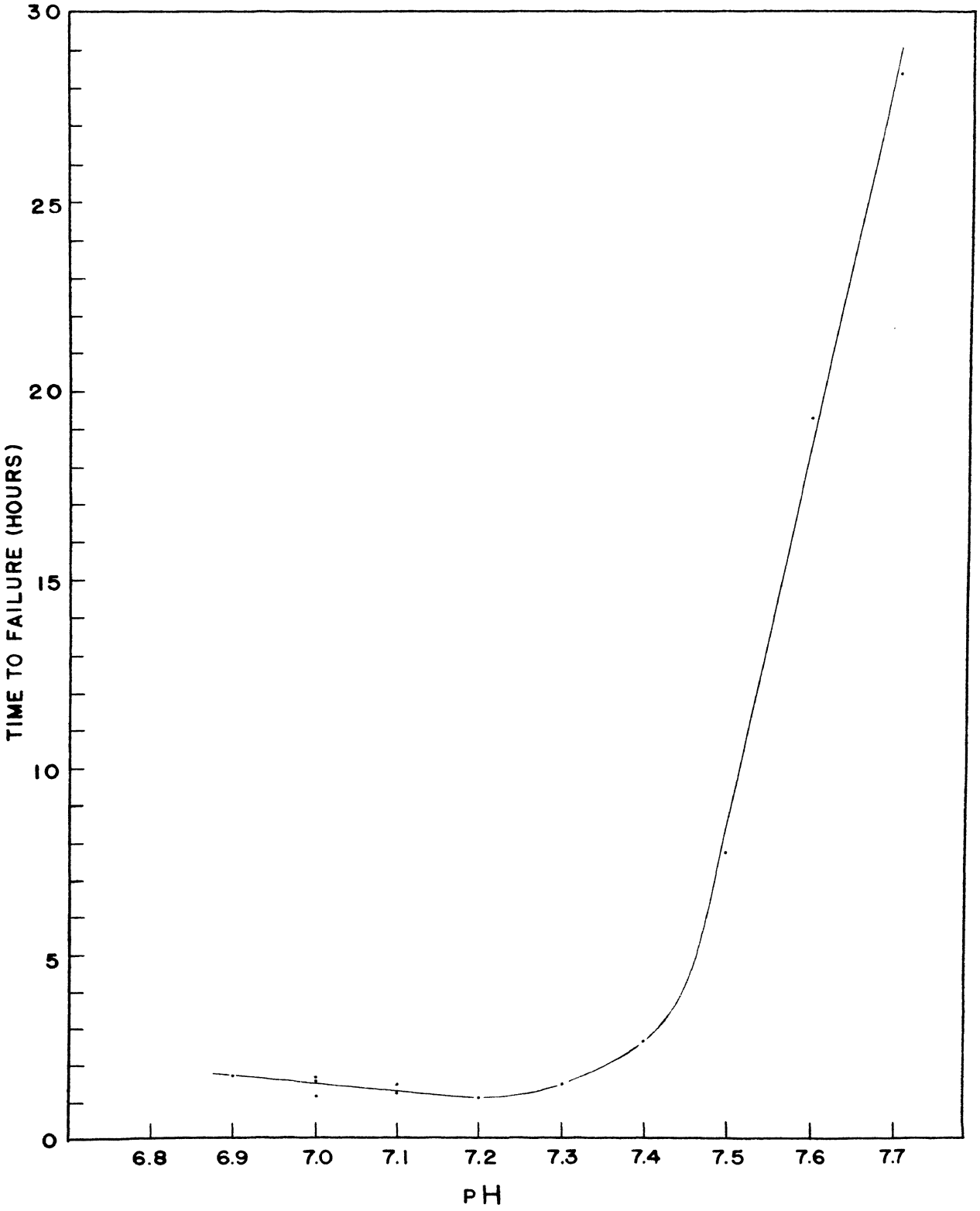

FIGURE 18

THE EFFECT OF pH ON
TIME TO FAILURE

B. Corrosion Medium

Solutions which had initial pH values of 6.5 through 7.2 experienced a change in pH and/or copper content as a result of the precipitation* which took place. Figure 19 shows the changes in copper content and pH during the period from the one hour check to the end of twenty-four hours. All percentages in the figure are based upon the original copper content of 0.05 gram atom of copper per liter. The upper point on each line indicates the pH and copper content of the solution one hour after preparation. The lower point shows the values after twenty-four hours of aging.

1. Copper in solution

The most immediate change in the pH 6.5-7.0 solutions was the loss of copper within the first hour after preparation, as shown in figure 19. During the next twenty-three hours, precipitation continued to take place and in all but three of these solutions it resulted in an additional

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* NOTE: An x-ray diffraction study was conducted on the precipitate and it indicated that the green material was a basic copper sulfate, $CuSO_4 . 3Cu(OH)_2$.

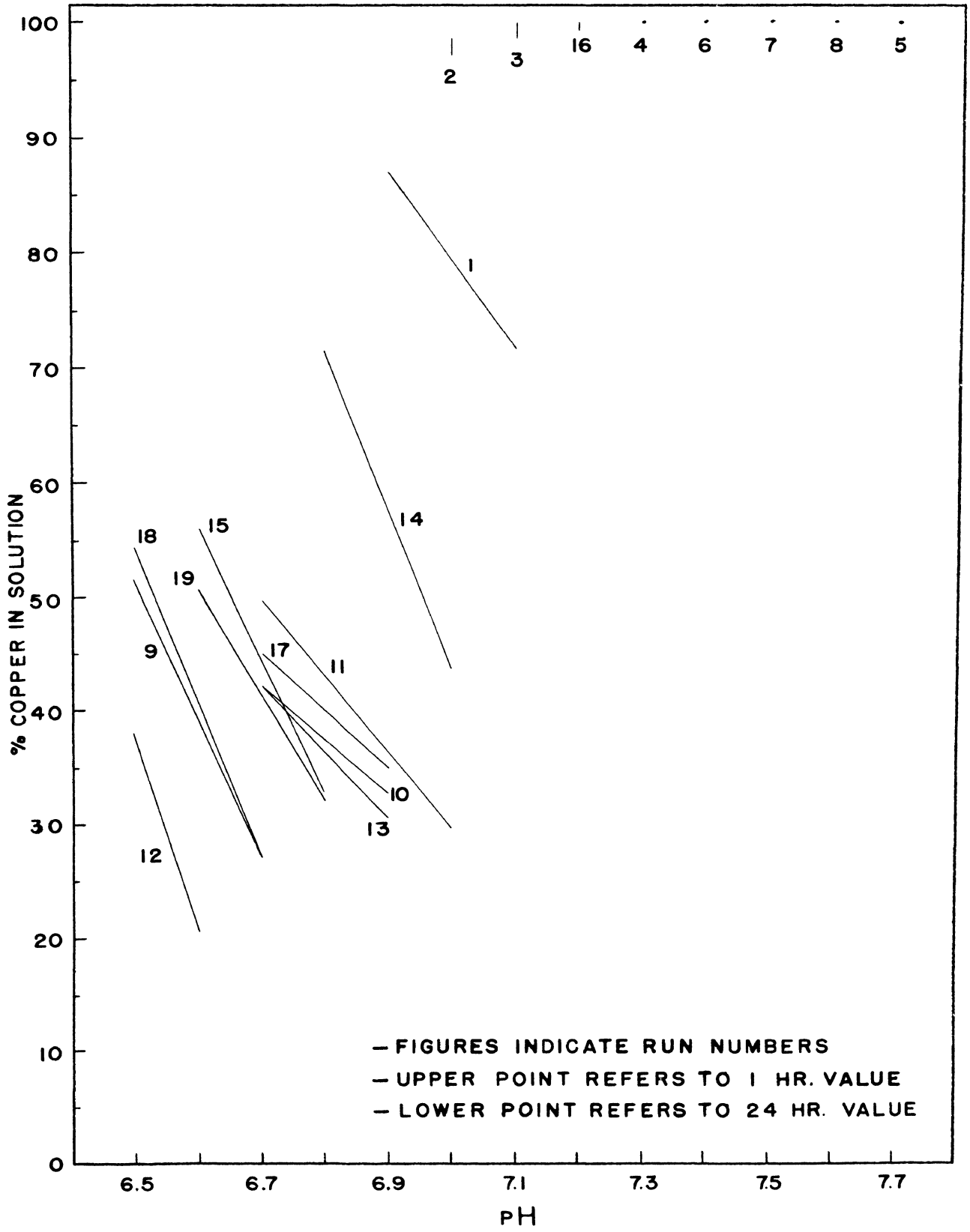

FIGURE 19

CHANGES IN THE SOLUTIONS
AS A RESULT OF AGING

copper loss amounting to ten percent or more. However, there was a sharp arrest in solution 2 (pH 7.0) where the total twenty-four hour loss was less than five percent as compared to the loss of almost thirty percent for solution 1 which had an initial pH of 6.9. Copper losses, although very small, occurred in solutions 3 (pH 7.1) and 16 (pH 7.2). Precipitation continued to take place after twenty-four hours although the rate of copper loss was lower.

2. pH

Referring to figure 19, it can be seen that all of the solutions on the acid side experienced a change in pH while aging. With the exception of solutions 11 and 12, they all gained 0.2 pH unit during this period. Solution 11, compared with solutions 10, 13, and 17, did not lose as much copper in the first hour, however, in the ensuing twenty-three hours it lost more copper than the others which accounted for the change of 0.3 pH unit. Solution 12 lost considerably more copper during the first hour than did solutions 9 and 18 but it did not subsequently lose as much copper in the aging period which followed and therefore it only underwent a change of 0.1 pH unit.

An abrupt stop in the trend observed, with regard to change in pH, occurred at pH 7.0 as did the rate of copper loss mentioned in the previous section. Solutions which were neutral or basic sustained no measurable change in pH during the storage period.

3. Results from similar solutions

Because the pH changed at a rate comparable with the loss of copper from solution it was possible to attain two solutions which exhibited the same pH after twenty-four hours of aging but which had different amounts of copper in solution. Referring to Table I, solution 1 had values, after one hour of aging, of 87.10 percent copper and pH 6.9. After twenty-four hours the respective values were 71.69 and 7.1. Solution 3 had initial values of pH 7.1 and 100 percent copper in solution whereas after twenty-four hours the copper content had only decreased to 98.74 percent while the pH remained at 7.1.

The data concerning time to failure and weight loss for these particular solutions could not be averaged since the specimens had been exposed to two completely different solutions. Therefore, the data for different solutions

which attained the same pH were treated separately when used to plot graphs.

C. Specimens

After the specimens were removed from the solution they were observed for (1) weight loss, (2) surface coatings, and (3) nature of cracking, if present.

1. Weight loss

Table I gives the average weight loss for each run in addition to the rate of weight loss. The latter values, which were obtained from all of the runs including those which did not produce time to failure measurements, are plotted in figure 20. Figure 21 is a graph of percent weight loss versus pH using data only from runs which gave indications of failure. In figure 20, the slope of the curve changes sharply in the vicinity of pH 6.9-7.0 and the slope of the curve in figure 21 deviates at approximately pH 7.4. Both of these changes correspond to other observations which will be discussed in other sections.

2. Surface coatings

In all but three tests, the specimens obtained a shiny,

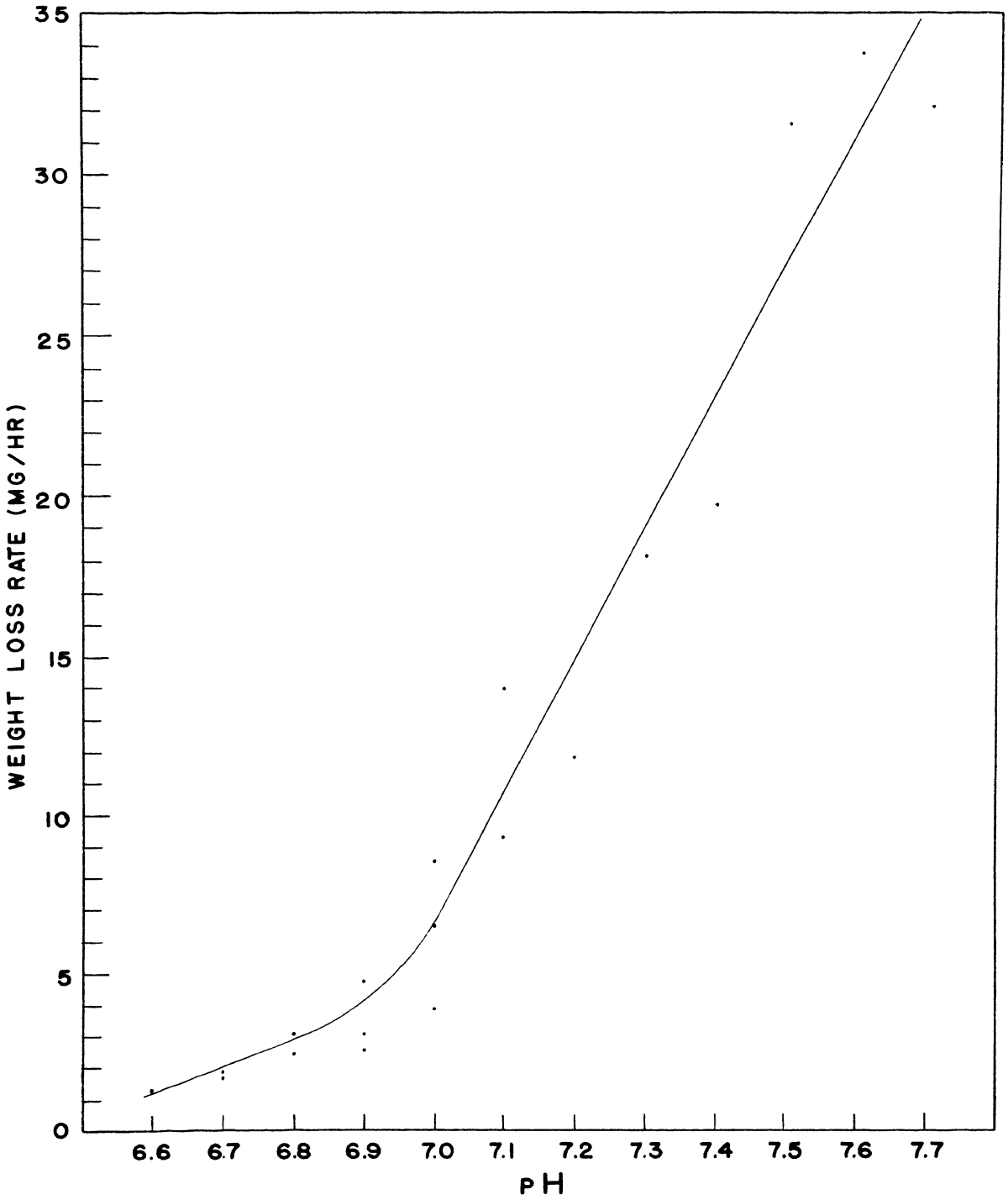

FIGURE 20

THE EFFECT OF pH ON RATE OF WEIGHT LOSS

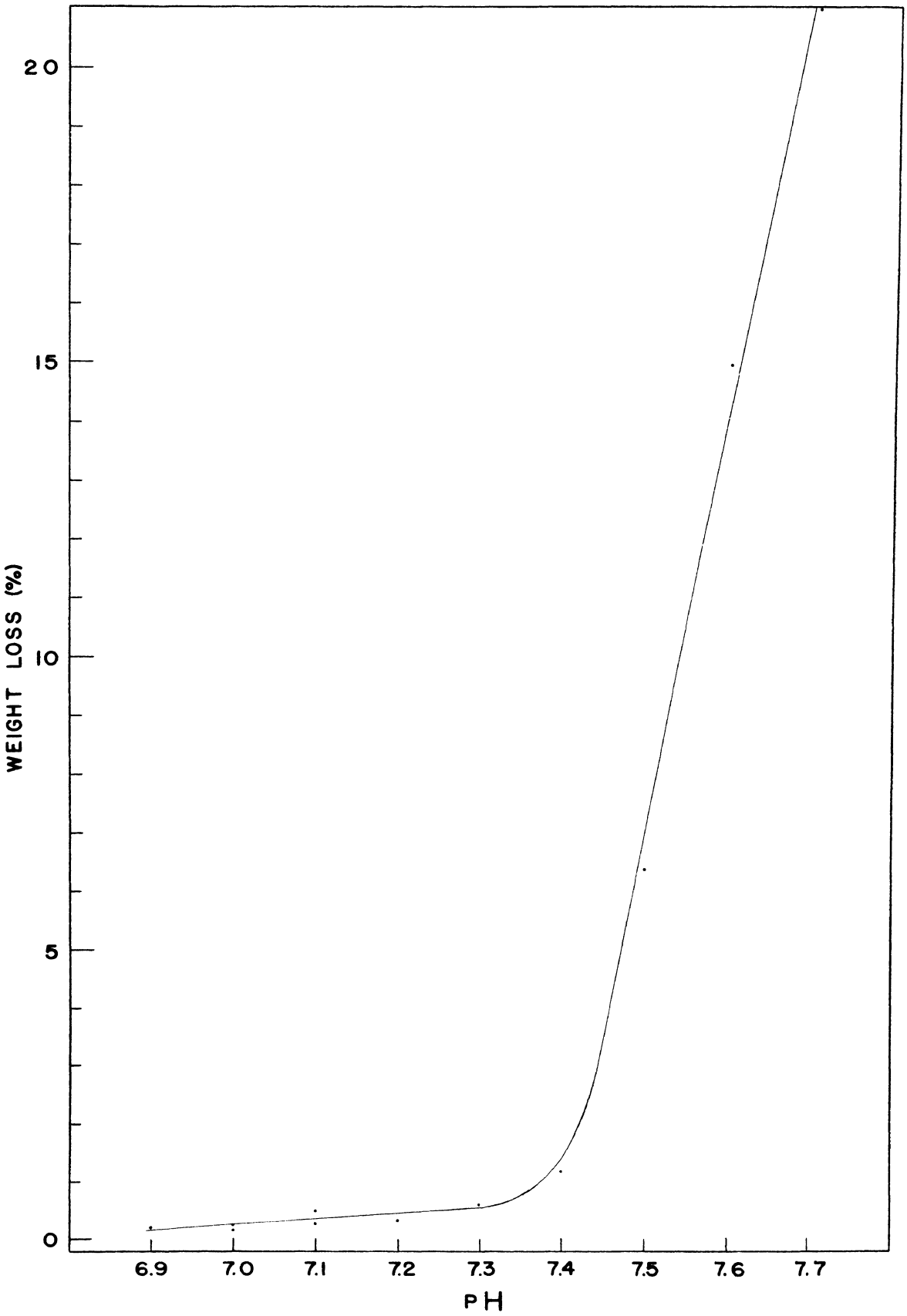

FIGURE 21

THE EFFECT OF pH ON PERCENT WEIGHT LOSS

black surface coating. The exceptions occurred in the pH 7.5-7.7 solutions. The coating for the 7.5 specimen was a very faint olive green color and the surface was smooth, but dull, in appearance. The 7.6 specimen had a gold colored silt present on it which was readily washed off by the rinse water. The new surface had a gold color and appeared to have a texture similar to fine abrasive paper. A gray silt was washed from the 7.7 specimen and revealed a multicolored surface with red, blue, and green colored stains present in addition to the same gold color and surface texture exhibited by the 7.6 specimen. The pH range where changes in surface appearance occurred corresponds with the sharp inflection shown in figure 21.

3. Cracking

As stated on page 41, time to failure measurements were obtained for solutions having pH values from 7.0-7.7. Also, one solution out of three having a pH of 6.9 produced failure.

Figures 22, 23, and 24 show three representative photomicrographs of specimens covering the pH range investigated. The specimen which was tested at pH 7.2 and which

FIGURE 22

THIN INTERGRANULAR CRACK PRESENT IN SPECIMEN FROM RUN 16, pH 7.2 (425X, $NH_4OH-H_2O_2$ ETCH)

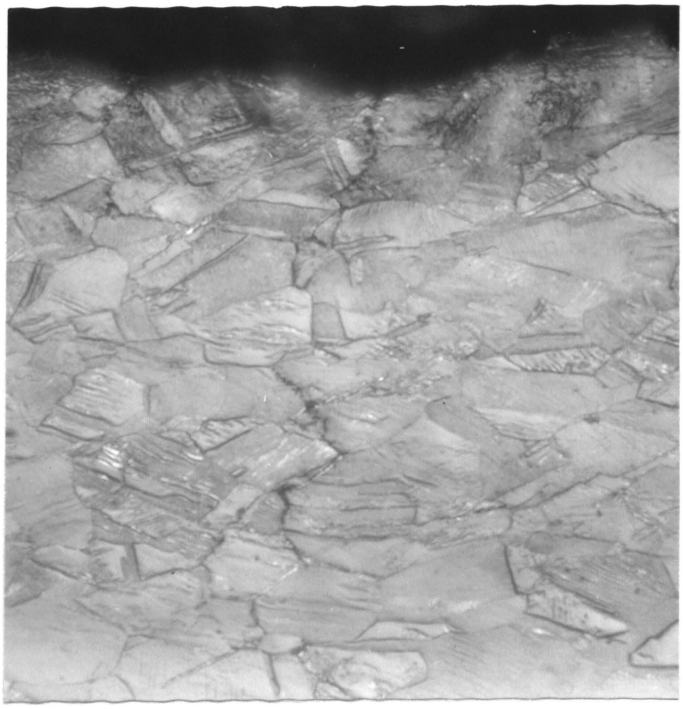

FIGURE 23

SPECIMEN FROM RUN 7, pH 7.5 WITH FINE INTERGRANULAR CRACK (500X, $NH_4OH-H_2O_2$ ETCH)

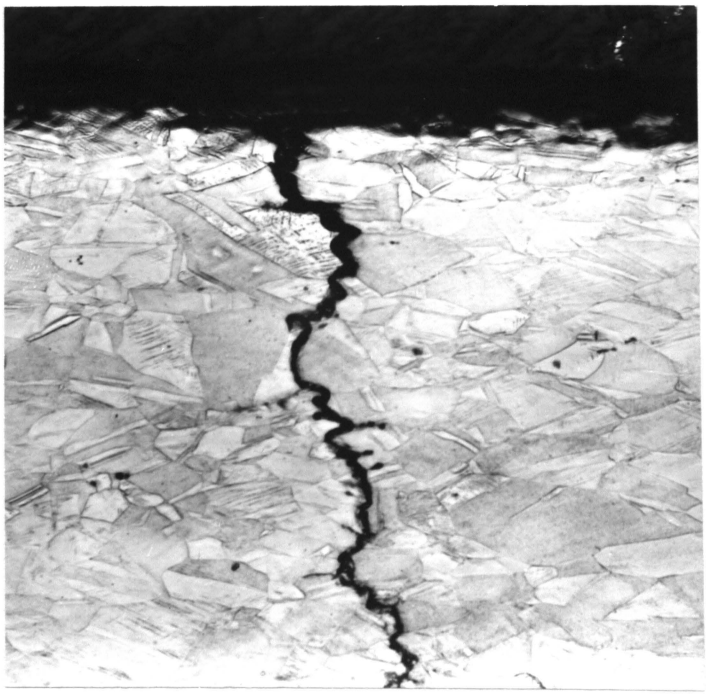

FIGURE 24

LARGE CRACK AND THICK BLACK COATING ASSOCIATED WITH SPECIMEN FROM RUN 12, pH 6.6 (300X, NH_4OH-H_2O_2 ETCH)

failed fastest shows a very fine crack in figure 22. Figure 23 shows a crack present in the specimen from run 7 (pH 7.5). This crack is less evident than the one at 7.2 even though the magnification has been increased.

The specimens from runs 5 (pH 7.7) and 8 (pH 7.6) showed no discernible cracking. The cracks, if present, were very fine and were not distinguishable from the grain boundaries. This is possible since the size of the cracks appeared to become smaller as the pH increased.

In figure 24 there appears to be a very large crack in the specimen. When compared to figures 22 and 23, with consideration given to their respective magnifications, it is quite large. However, the specimen did not give an indication of failure in 48 hours of exposure. When the specimen was observed microscopically, the crack appeared to be filled with material having the same appearance as the coating.

In the previous section, mention was made of the fact that in the majority of the runs the specimens obtained a black coating. This coating varied in thickness, however, and was greatest in the range from pH 6.6-6.9.

Aside from the thick coating, figure 20 on page 49 shows that the rate of weight loss experienced by the specimens in the pH 6.6-6.9 range was very low compared with the rate indicated by specimens in the 7.1-7.3 range which failed quickly. When the overall weight losses were compared the 6.6 specimen lost approximately five times as much weight as did the 7.2 specimen while it was exposed almost fifty times as long.

Because of this small comparative weight loss and no indication of failure, it was assumed that the black coating had a bearing on the apparent strength of the specimen. It was also assumed that when the specimen was initially immersed in a solution having a pH in the range from 6.6-6.9, the precipitation, which was still taking place, prohibited immediate initiation of cracking. Instead, it allowed the surface coating to form to such an extent that it would not fracture under the force of the apparatus.

Because of the sudden changes in the properties of the solutions at pH 7.0, as discussed on pages 44 and 46, the coating did not have a chance to become so thick that it could not be fractured by the opposing force of the apparatus. This border line was also distinguished by the

time to failure data from the pH 6.9 solutions in which one-half of the specimens failed and the other half did not indicate failure in forty-eight hours.

In all of the runs, the cracking which took place was intergranular, as shown in figures 22, 23, and 24. Transgranular cracking, although it is less common, can be produced. Figure 25 shows a transgranular crack which was obtained in a preliminary run by exposing the specimen to ammonia vapors rather than immersing it. Smaller cracks present in the figure are also transgranular.

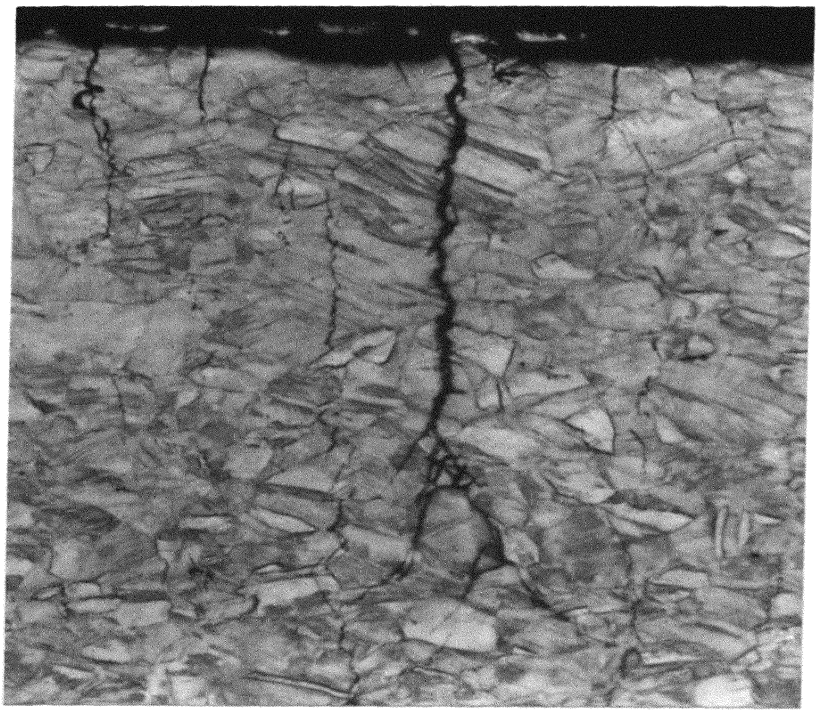

FIGURE 25

TRANSGRANULAR CRACKS FORMED BY EXPOSING SPECIMEN TO AMMONIA VAPORS

V. SUMMARY

A. Apparatus

The primary objective, for which the apparatus was built, was attained. It was able to detect the failure of the specimens, as a result of their cracking, and did it by assessing their strength which is a quantitative measure rather than qualitative.

Since the specimens were prepared in the same manner and had dimensions which were duplicated as closely as possible, the initial strengths of the specimens could be assumed as being nearly equal.

The initial adjustments made on the apparatus' linkage were not changed throughout the study so that each specimen was subjected to the same conditions, aside from the solution, and the indication of its failure was based on its strength decreasing by a certain amount.

The functioning of the apparatus was observed during the study and only one significant problem was encountered. If the apparatus was subjected to considerable shock it caused a premature indication of specimen failure. This

was because of the manner in which the apparatus was constructed. The stainless steel rods and pivot housings moved downward in a normal failure. Any shock which caused a rapid displacement of the whole apparatus, downward, caused these heavy items to receive enough momentum to trigger the microswitches. Typical instances which caused premature indications of failure during this study were slamming of nearby doors, vibrations due to heavy equipment being used close by, and bumping the cabinet which housed the apparatus. With the exception of jarring the cabinet, all of these probably could have been eliminated if a lighter cabinet had been utilized. The cabinet which was used was quite heavy and even though it was sitting on rubber mats it still transmitted, to the apparatus, a large portion of the shock received.

B. Corrosion Medium

The time to failure of the brass specimens was found to be dependent upon the pH of the solution. This observation is more correctly confined to the range from pH 7.0 through 7.7 since pH was the primary variable which changed to any extent. In the solutions having pH values from 6.6 through 6.9, the copper content and pH both changed

to a large degree. The loss of copper occurred as a result of the precipitation which took place from the time of mixing until well after the specimens were tested. Because of this the specimens did not give indications of failure except in a few instances at pH 6.9. This is the reason for the difference between the time to failure plot resulting from this study (figure 18, page 43) and Mattsson's plot (figure 2, page 15). The data which he used resulted from solutions which had aged for forty-eight hours. The extra twenty-four hours allowed the solutions which experienced precipitation to become more stable.

The following items, the amount of copper lost from the solutions, the ability to repeat time to failure measurements, and the rate of weight loss from the specimens, all underwent a sudden change between pH 6.9 and 7.0. The specimens showed no visible change with regard to surface coatings in this pH range.

The surface coatings did change, however, at pH 7.5 which was confirmed by the percentage of weight lost by the specimens. They changed from hard, shiny surfaces to rough textured surfaces covered with a "silt" layer which was a corrosion product.

Because of the large weight losses, the change in surface coatings, and the absence of discernible cracks, the indicated failures given by the pH 7.6-7.7 specimens could initially be attributed to their weakening because of a reduction in cross sectional areas by general corrosion. However, when figures 18 and 21 (pages 43 and 50, respectively) are compared it can be seen that the increase in percent weight loss corresponds with an increase in time to failure throughout the range in question. The fact that the specimens had different weight losses would tend to disprove this initial concept since essentially the same amount of material would have to be lost to give an equivalent reduction in area.

One run was conducted at pH 8.6 and showed a time to failure of 3.76 hours. This is in agreement with Mattsson's curve (figure 2, page 15). Due to lack of time for other runs in the pH range 8.0-9.0, these data were not included in Table I.

VI. CONCLUSIONS

A. Apparatus

Failure in a u-bend specimen, as a result of stress corrosion cracking, can be detected by the apparatus used in this study. Instances such as that encountered in this study in which a surface coating restricted the specimen from indicating failure are exceptions.

In a range of pH values where times to failure are very close the apparatus is capable of recording times accurately enough to establish a true minimum.

The accuracy of other data, such as rate of weight loss, is a result of the more accurate time to failure measurements.

B. Corrosion Medium

From this study it was concluded that the pH of the ammoniacal copper sulfate solution had a considerable affect on the time to failure of the brass specimens.

Also, the precipitation, which occurred to the greatest extent on the acid side, had a great influence on the speed with which the initiation of cracks took place.

VII. SUGGESTED FURTHER RESEARCH

The apparatus shows considerable versatility since it is not limited to testing any one material provided the specimen's strength, when bent, is within the range of the linkage adjustments.

It is suggested that other metals together with other types of corrodents be studied. The use of other corrodents with this apparatus is virtually unlimited provided the stainless steel is not attacked in the process.

Also, with very little work it could be arranged so that anodic and cathodic polarization of the specimens could be studied while the characteristics of the corrosion medium remain constant throughout the study.

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APPENDIX A

Calculations Used in the Preparation of Solutions

The table of specific gravity versus percent ammonia for ammonium hydroxide[23] shows the value of 0.9500 to be between 0.9492 and 0.9508 which correspond to 13.02 and 12.56 percent ammonia, respectively. By interpolation it is found;

$$\frac{0.9508 - 0.9500}{0.9508 - 0.9492} = \frac{12.56 - x}{12.56 - 13.02}$$

$$-0.23 = 12.56 - x$$

$$x = 12.79 \text{ gm } NH_3/100 \text{ gm of solution}$$

From the table giving the density of water at various temperatures[24] it was found that at 25°C the density of water is 0.99707 gm/ml. By using this value the density of the ammonium hydroxide was calculated and found to be 0.9472 gm/ml.

$$\frac{12.79 \text{ gm } NH_3}{100 \text{ gm of soln.}/0.9472 \text{ gm/ml}} = 0.1211 \text{ gm } NH_3/\text{ml}$$

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[23] Norbert Adolph Lange (comp. & ed.), Handbook of Chemistry (seventh edition; Sandusky, Ohio: Handbook Publishers, Inc., 1949) p. 1281.

[24] Ibid., pp. 1385-6.

In calculating the amount of ammonium sulfate necessary to complete the one gram mole of ammonia per liter the following equation was utilized.

$$2\ NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

For example, 88.9 milliliters of ammonium hydroxide were to be used in the preparation of one of the solutions.

$$88.9\ ml \times 0.1211\ gm\ NH_3/ml = 10.77\ gm\ NH_3$$

$$\begin{array}{r} 54.50\ gm\ NH_3, \text{ total} \\ -\underline{10.77}\ gm\ NH_3 \text{ added as } NH_4OH \\ 43.73\ gm\ NH_3 \text{ necessary as } (NH_4)_2SO_4 \end{array}$$

$$\frac{\dfrac{43.73\ gm\ NH_3}{17.03\ gm\ NH_3}}{\text{gm-mole } NH_3} \times \frac{1\ \text{gm-mole } (NH_4)_2SO_4}{2\ \text{gm-mole } NH_3} = \frac{X}{\dfrac{132.14\ gm\ (NH_4)_2SO_4}{\text{gm-mole } (NH_4)_2SO_4}}$$

$$X = 169.65\ gm\ (NH_4)_2SO_4$$

APPENDIX B

TABLE II

METALLOGRAPHIC REAGENTS

Polishing Reagent

$FeCl_3$ - - - - 5 gm

Methanol - -96 ml

HCl (conc) - 2 ml

Etching Reagents

Hydroxide-peroxide

NH_4OH (conc) - - 7 ml

H_2O_2(3%) - - - - 3 ml

Ferric chloride

$FeCl_3$ - - - - 19 gm

H_2O - - - - -100 ml

HCl (conc) - 6 ml

VITA

Floyd Elwin Loftin was born in Altamont, Illinois on August 17, 1939. He received both his elementary and high school education in Altamont. He enrolled at Missouri School of Mines and Metallurgy in September 1957 and received his B.S. degree in Metallurgical Engineering in May 1961. Having also received his Reserve Commission upon graduation he immediately entered the U.S. Army and served during the period from July 1961 to July 1963. He enrolled in the School of Mines and Metallurgy of the University of Missouri at Rolla in September 1963 and began the research work presented here.